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Accepted Version

Van Den Hoof, C. and Thiry, Y. (2012) Modelling of the natural chlorine cycling in a coniferous stand: implications for chlorine-36 behaviour in a contaminated forest environment. *Journal of Environmental Radioactivity*, 107. pp. 56-67. ISSN 0265-931X doi: <https://doi.org/10.1016/j.jenvrad.2011.12.014> Available at <https://centaur.reading.ac.uk/26017/>

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Published version at: <http://www.sciencedirect.com/science/article/pii/S0265931X11003092>

To link to this article DOI: <http://dx.doi.org/10.1016/j.jenvrad.2011.12.014>

Publisher: Elsevier

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Modelling of the Natural Chlorine Cycling in a Coniferous Stand: Implications for Chlorine-36 Behaviour in a Contaminated Forest Environment

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Abstract

Considered as one of the most available radionuclide in soil-plant system, ^{36}Cl is of potential concern for long-term management of radioactive wastes, due to its high mobility and its long half-life. To evaluate the risk of dispersion and accumulation of ^{36}Cl in the biosphere as a consequence of a potential contamination, there is a need for an appropriate understanding of the chlorine cycling dynamics in the ecosystems. To date, a small number of studies have investigated the chlorine transfer in the ecosystem including the transformation of chloride to organic chlorine but, to our knowledge, none have modelled this cycle. In this study, a model involving inorganic as well as organic pools in soils has been developed and parameterised to describe the biogeochemical fate of chlorine in a pine forest. The model has been evaluated for stable chlorine by performing a range of sensitivity analyses and by comparing the simulated to the observed values. Finally a range of contamination scenarios, which differ in terms of external supply, exposure time and source, have been simulated to estimate the possible accumulation of ^{36}Cl within the different compartments of the coniferous stand. The sensitivity study supports the relevancy of the model and its compartments and has highlighted the chlorine transfers affecting the most the residence time of chlorine in the stand. Compared to observations, the model simulates realistic values for the chlorine content within the different forest compartments.

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For both atmospheric and underground contamination scenarios most of the chlorine can be found in its organic form in the soil. However, in case of an underground source, about two times less chlorine accumulates in the system and proportionally more chlorine leaves the system through drainage than through volatilisation.

Keywords: Chlorine cycles, Coniferous forest, Modelling, Contamination assessment.

1. Introduction

Chlorine is a wide-spread element in natural environments. It is considered as one of the more mobile elements in soil and is also an essential micronutrient for higher plants (White and Broadley, 2001). Chlorine occurs in nature as two stable isotopes; chlorine-35 and chlorine-37 with ^{35}Cl being the most prevalent. Of the seven radioactive chlorine isotopes, only one, chlorine-36, has a half-life longer than 1 hour. ^{36}Cl decays with a half-life of 300,000 years by emitting a beta particle and electron capture; most of the decays (98%) are by beta-particle emission. ^{36}Cl is generated naturally by spallation in the atmosphere of argon-36 by cosmic ray protons, by interactions between cosmic radiation and Cl, Ca and K in near-surface rocks and soils, and by neutron activation of ^{35}Cl in soil and rock (White and Broadley, 2001). ^{36}Cl is also produced anthropogenically during nuclear tests and nuclear industrial processes; i.e. ^{36}Cl is produced by neutron activation of ^{35}Cl present in materials used in nuclear reactors. As a consequence, waste fuel and certain construction materials originating from dismantling nuclear installation might contain ^{36}Cl . Its mobility combined with its long half-life thus makes ^{36}Cl a radionuclide of potential concern for long-term management of radioactive wastes. High mobility in the soil column and a ready availability in soil solution (Ashworth and Shaw, 2006) allow ^{36}Cl to potentially contaminate the biosphere easily. Considered as one of the most available radionuclide for plants (Colle et al., 2002), ^{36}Cl was shown to have the same behaviour as stable Cl in soil and plants (Kashparov et al., 2007). Consequently, radio-chlorine is likely to be recycled in the biosphere and impact the food chain over a very long time.

Because chloride (Cl^-), its widespread anionic form, has few affinities for the soil solid phase, chlorine is often considered as a conservative tracer of

soil water movements with no implication in biological processes. While this view is valid in deep geological layers, it is questioned when considering surface soils due to the thousands of chlorinated organic compounds that are produced naturally in the biosphere (Winterton, 2000). The natural chlorination of soil organic matter (SOM) through biotic processes (Bastviken et al., 2009) seems largely responsible of the formation of organochlorine which was found to accumulate in large amount in certain organic soils e.g. coniferous forest (Redon et al., 2011). In many cases, the organic chlorine pool is often greater than the inorganic pool. In fact, the natural cycle of chlorine in soils is complex involving simultaneous formation and degradation of chlorinated organic compounds but attempts to rationalise sources and fluxes of organic and inorganic chlorines in soils are still scarce (Clarke et al., 2009). To evaluate the risk of dispersion and accumulation of ^{36}Cl in the biosphere due to a potential atmospheric or underground contamination, there is a need for an appropriate understanding and modelling of the chlorine cycling dynamics in a range of representative ecosystems.

The objective of this study is to develop a model describing the biogeochemical fate of chlorine in a coniferous forest based on measurements of stable chlorine performed in a pine forest around Mol (Belgium). During the measurements particular attention has been paid to the partitioning of the organic and inorganic chlorine into the different compartments of the ecosystem to better evaluate the contribution of the organic chlorine formation to the accumulation of chlorine within the ecosystem. Since ^{36}Cl has the same behaviour as stable chlorine in soils and plants, this model was then used as a questioning tool to estimate, under a range of contamination scenarios, the possible redistribution of ^{36}Cl between the different forest compartments.

2. Materials

2.1. Study area and measurements

The experimental Scots pine (*Pinus sylvestris* L.) stand is located at Mol in the Belgian Campine region. The local area has a rural and forested character with a high proportion of humid soils and wet zones. The topography is flat and the altitude is 15 m. The 60 year old stand is part of a 189 ha forest dominated by Scots pine, with some patches of oak trees. In 2004, the stand density was 359 trees ha^{-1} . The mean height, circumference (at 1.3 m) and

stand basal area of the Scots pine were respectively 22 m, 0.91 m and 24.4 m². In addition to grasses and mosses, the understorey vegetation mainly consists of *Sorbus aucuparia*, *Prunus serotina*, *Rubus sp* and *Athyrium filix femina*. The soil is a podzol and is classified as a distric Cambisol. The water table depth is very shallow. It fluctuates between 1.2 m to 0.5 m during spring and shows very strong intra-seasonal variations. A detailed description of the site can be found in Vincke and Thiry (2008).

During 2005 and 2006, a large number of soil and vegetation samples have been collected at this site. These samples were used to determine vegetation biomass and soil mass, as well as the levels of organic and inorganic chlorine in different compartments of the ecosystem. The chlorine content has been determined using the Neutron Activation Analysis technique. The procedures to differentiate the organic and inorganic chlorine content within the soil and vegetation samples have been adapted from Öberg et al. (2005). During the sampling campaign, the following items have been collected: water (precipitation and through-fall), tree (needles of one year and older, twigs, branches, wood, bark, roots), understorey (grasses, mosses, shrubs, ferns, fungi, berries) litter-fall (needles, bark, branches), and organic and mineral soil layers. The sampling procedures have been described in detail by Van Hees and Vandenhove (2009). In addition to a chlorine budget, the biological cycling dynamics in the pine stand was quantitatively described in terms of annual fluxes based on annual biomass production and respective average chlorine concentrations in the various tree compartments (Thiry, 2010). The calculations used to assess the element cycling were described in Goor and Thiry (2004).

2.2. Speciation and distribution of chlorine in soil and vegetation

In the pine stand, which is characterised by an atmospheric deposition of 12.6 kg ha⁻¹ yr⁻¹ of stable chlorine, a quantitative description of the chlorine budget and cycle resulted in the following conclusions (Thiry, 2010):

- The accumulation of chlorine in the soil at the pine stand is linked to the formation of organic chlorine. The transformation of inorganic to organic chlorine takes place once the decomposition of the humus has started in the O_f layer. Under our conditions, the rate of organic matter chlorination is estimated around 0.62 kg Cl ha⁻¹ yr⁻¹. 80%

of the transformed inorganic chlorine originates from wet depositions. In the whole soil profile the concentration of organic chlorine is 3 to 4 times larger than the concentration of inorganic chlorine.

- Within the different tree compartments, the foliage has the largest chlorine concentration ($590 \mu\text{g Cl g}^{-1} \text{ d.m.}$), accounting for roughly 35% of the total chlorine present in the tree. More than 90% of the chlorine in the leaves and the bark is in its inorganic form. This highlights the high chlorine mobility in the tree. The higher concentration of chlorine in the leaves compared to the soil ($27\text{-}279 \mu\text{g g}^{-1}$) can be explained by the selective uptake of chlorine by the vegetation. On average, 20% of the chlorine present in the whole tree is in its organic form.
- The annual uptake of chlorine through root absorption is nine-fold larger than the chlorine demand by the tree, which is the total quantity of element mobilised by the current production of biomass (Goor and Thiry, 2004). This uptake takes place at a rate equivalent to the atmospheric deposition. The excess of chlorine is removed from the tree and returned to the soil through internal transfers at leaf level and subsequently through-fall. Under our conditions, litterfall plays a minor role in Cl return to the soil.
- The chlorine content within the tree biomass represents only 0.9% of the total chlorine content present in the whole pine stand. The chlorine content in the understorey and in the root system cannot be neglected since they represent respectively 1.2% and 0.5% of the total chlorine within the ecosystem at the stand. Most of the chlorine can be found in the forest floor (5.7%) and in the mineral soil layer (91.7%).
- Assuming that the system is in equilibrium, the residence time of chlorine was estimated based on a mass balance. In the tree the residence time is very short; i.e. 0.4 years. The residence time is longer in the forest floor and in the soil, respectively 3 and 47 years. The residence time of chlorine in the soil seems to be mainly regulated by the dynamics of the chlorination of organic matter and the biodegradation of organo-chlorinated compounds. The residence time of chlorine in the whole system is 48 years.

3. Methods

3.1. Model development

In this study, the cycling of chlorine in the coniferous stand is represented by a seven-compartment model consisting of a mineral soil subdivided into an organic (C_1) and inorganic (C_2) chlorine pool, a forest floor component subdivided as well into organic (C_4) and inorganic (C_3) chlorine pool, a root component (C_5), an above-ground tree component (wood and leaves, C_6) and a leaf surface component (C_7). The drainage from the top 110 cm of the soil (C_8) and the volatilisation (C_9), both accounting for losses of chlorine out of the system, are identified as the eighth and ninth compartments. The chlorine input through atmospheric (C_{10}) or underground supply (C_{11}) are defined as the tenth and eleventh compartments. A conceptual scheme of the model is represented in Figure 1. This model structure is similar to that of models developed for forest ecosystems and radionuclides expected to interact with organic matter (Garten, 1978, 1987).

The above-mentioned compartments are interconnected by chlorine fluxes expressed in terms of fractions and transfer rates, $k_{i,j}$. Each flux rate represents the fractional transfer of chlorine from compartment i to compartment j . Nine flux rates were used to identify the chlorine cycling in the ecosystem. In addition to this, the atmospheric deposition on the external leaf surface ($k_{10,3}$) and on the forest floor ($k_{10,7}$), and the underground source ($k_{11,1}$) were identified as the tenth, eleventh and twelfth fluxes. The change in the amount of chlorine over time in the different compartments is expressed as:

$$\frac{dC_i}{dt} = \sum_i (\text{inputs to } C_i) - \sum_i (\text{outputs from } C_i) \quad (1)$$

Based on Equation 1, the chlorine transfer between the different compartments can be determined by solving the following set of first-order linear differential equations:

$$\frac{dC_1}{dt} = k_{11,1}C_{11}e^{-t/T_{sc}} + k_{5,1}C_5 + k_{2,1}C_2 + k_{3,1}C_3 - (k_{1,5} + k_{1,8})C_1 \quad (2)$$

$$\frac{dC_2}{dt} = k_{5,2}C_5 + k_{4,2}C_4 - (k_{2,8} + k_{2,1})C_2 \quad (3)$$

$$\frac{dC_3}{dt} = k_{5,3}C_5 + k_{6,3}C_6 + k_{7,3}C_7 + k_{10,3}C_{10} - (k_{3,5} + k_{3,1} + k_{3,4})C_3 \quad (4)$$

$$\frac{dC_4}{dt} = k_{6,4}C_6 + k_{3,4}C_3 + k_{5,4}C_5 - (k_{4,2} + k_{4,9})C_4 \quad (5)$$

$$\frac{dC_5}{dt} = k_{6,5}C_6 + k_{3,5}C_3 + k_{1,5}C_1 - (k_{5,6} + k_{5,3} + k_{5,4} + k_{5,1} + k_{5,2})C_5 \quad (6)$$

$$\frac{dC_6}{dt} = k_{7,6}C_7 + k_{5,6}C_5 - (k_{6,5} + k_{6,4} + k_{6,3})C_6 \quad (7)$$

$$\frac{dC_7}{dt} = k_{10,7}C_{10}e^{-t/T_{ac}} - (k_{7,3} + k_{7,6})C_7 \quad (8)$$

$$\frac{dC_8}{dt} = k_{1,8}C_1 + k_{2,8}C_2 \quad (9)$$

$$\frac{dC_9}{dt} = k_{4,9}C_4 \quad (10)$$

where T_{sc} and T_{ac} are soil and atmosphere contamination/exposure time scales, respectively. For simulation with a constant level of contamination/exposure, $e^{-t/T_{sc}}$ and $e^{-t/T_{ac}}$ are set equal to 1. The dimensioning of the model complexity was mainly set by the availability of data; i.e. measured or extracted from literature. The number of compartments and fluxes was assumed to be optimal for a realistic representation of the main chlorine pools in the forest stand.

In the model, the transfer rates can be defined either as deterministic or as following a (normal) probabilistic distribution with a given arithmetic mean and standard deviation. In the former case, the model is non-stochastic, while in the latter case the model is stochastic. With a stochastic model, ensemble simulations can be performed to investigate the model sensitivity to initial parameter values or temporal variability in parameter values. All fluxes between compartments could not be measured and were thus deduced based on reasonable hypothesis. The mean values attributed to these transfer rates are discussed in Section 3.2. Finally, the model has been developed based on a range of assumptions:

- The forest stand is in equilibrium.
- The behaviour of ^{36}Cl is similar to the behaviour of stable chlorine
- The transfer rates are time-independent.

- The fluxes between compartments are controlled by the chlorine content in the donor compartment.
- As an initial condition, all the model compartments are assumed to be empty.

3.2. Model parameterisation

Fraction of atmospheric deposition onto leaf surface (k_{10-7}) and forest floor - inorganic Cl pool (k_{10-3}) The interception fraction of chlorine present in wet deposits is assumed to be equal to the interception fraction of the precipitation by the canopy. In the pine stand it is around 0.29 (Vincke and Thiry, 2008). This implies a value of 0.71 for the fraction not retained by leaf surface.

Fraction transferred from leaf surface to above-ground tree biomass (k_{76}) This transfer corresponds to the translocation of an element deposited on the plant surface to other parts that were not directly exposed to the atmospheric deposition. A value of 0.15 was assigned to the parameter k_{76} . This relatively high value was selected in the light of recent field experiments on ^{36}Cl translocation in plants (Hurtevent et al., Submitted).

Fraction leached from leaf surface to forest floor - inorganic Cl pool (k_{73}) The process of canopy weathering is the loss of material from leaf surface after wet deposition. Given the high solubility of chlorine, primarily as Cl^- anion in atmospheric deposition (Öberg et al., 2005; Winterton, 2000), it is assumed that the residual deposits i.e. not absorbed within the foliage, are rapidly and efficiently removed through washing and leaching. A value of 0.845 was assigned to the parameter k_{73} , supposing that a small fraction of 0.005 could accumulate on the leaf surfaces.

Transfer from tree to forest floor - organic Cl pool (k_{64}) The transfer of organic chlorine from tree to forest floor is assumed to be equal to the fraction of the organic chlorine content in the annual litterfall, $0.099 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Thiry, 2010) and the total chlorine content in the pine tree, 5.5 kg ha^{-1} (Thiry, 2010). This leads to an average transfer rate of $4.93 \times 10^{-5} \text{ d}^{-1}$.

219 **Leaching from tree to forest floor - inorganic Cl pool (k_{63})** In
 220 the pine stand, the mobilisation of chlorine via crown leaching is equal to
 221 $13.27 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Thiry, 2010). Given a total chlorine content of 5.5 kg
 222 ha^{-1} in the above-ground biomass, the leaching rate is estimated to be equal
 223 to $6.61 \times 10^{-3} \text{ d}^{-1}$.

224
 225 **Transfers from the inorganic to the organic chlorine pool of the**
 226 **forest floor (k_{34})** In the top layers of a forest soil, the transformation of
 227 inorganic to organic chlorine is mainly due to natural processes of organic
 228 matter chlorination (Bastviken et al., 2009). Therefore, the transfer rate k_{34}
 229 was calculated based on the estimated chlorination rate and on the amount
 230 of inorganic chlorine measured in the O_f layer, which is around 2.6 kg ha^{-1} .
 231 As mentioned in Section 2.2, the chlorination rate at the pine stand was es-
 232 timated to be $0.62 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at the pine stand. This resulted in a value
 233 of $6.575 \times 10^{-4} \text{ d}^{-1}$ for k_{34} .

234
 235 **Transfers from the organic to the inorganic chlorine pool of the**
 236 **soil (k_{21})** There is a lack of information on the dynamics of Cl in or-
 237 ganic matter of forest soils in general and on the biological degradation of
 238 organically bound chlorine in particular (Clarke et al., 2009). However, de-
 239 grading organic matter seems to be a major source of inorganic chlorine
 240 in runoff (Lovett et al., 2005). A tentative balanced chlorine budget for a
 241 small forested catchment in Sweden (Öberg et al., 2005) suggested that a net
 242 mineralisation of organic chlorine takes place in soils, preferably in deeper
 243 mineral layers. In that study, the net mineralisation rate was estimated to be
 244 comparable to the rate of chlorination that is predominating in the top soil.
 245 Given a chlorination rate of $0.62 \text{ kg ha}^{-1} \text{ yr}^{-1}$, the degradation of organic
 246 chlorine to the inorganic form was estimated to be $4.22 \times 10^{-3} \text{ d}^{-1}$. This
 247 value is the ratio between the mineralisation rate and the organic chlorine
 248 content of the soil, which is equal to 401 kg ha^{-1} (Thiry, 2010).

249
 250 **Transfers of inorganic chlorine from the forest floor to the soil**
 251 **(k_{31})** The transfer rate k_{31} was assumed to be equal to the leaching rate
 252 ρ , which has been estimated based on the formulations of Hillel (1998) and
 253 Holmberg et al. (1989):

$$\rho = \frac{Q \times K(\theta)}{Z \times \theta} \quad (11)$$

254 where Q is the annual percolation, $K(\theta)$ the hydraulic conductivity, Z
 255 the soil layer thickness and θ the volumetric soil moisture content in this
 256 soil layer. In the pine stand, the forest floor is 81 mm thick (Thiry, 2010).
 257 An average value of 0.15 was assigned to the volumetric soil water content θ
 258 (Vincke and Thiry, 2008). During the same year, the top soil layer percolation
 259 Q was estimated at 453 mm yr⁻¹ (Vincke and Thiry, 2008), based on a
 260 precipitation rate (P) of 815 mm yr⁻¹, a top canopy evaporation (E_{can}) of
 261 232 mm yr⁻¹ and an understorey transpiration (T_u) of 130 mm yr⁻¹ ($Q =$
 262 $P - E_{can} - T_u$). The hydraulic conductivity $K(\theta)$ at the pine stand has been
 263 defined based on the conductivity at saturation $K(\theta_{sat})$ and the Mualem
 264 (1976)'s model for predicting the relative hydraulic conductivity $K_r(\theta)$ from
 265 knowledge of the soil-water retention curve:

$$K(\theta) = K_r(\theta) \times K(\theta_{sat}) \quad (12)$$

$$K_r(\Theta) = \bar{\Theta}^{1/2} (1 - (1 - \bar{\Theta}^{1/m})^n)^2 \quad (13)$$

266

267 with m and n the dimensionless Mualem-van Genuchten parameters, and
 268 $\bar{\Theta}$ a dimensionless water content defined as:

$$\bar{\Theta} = \frac{(\theta - \theta_r)}{(\theta_s - \theta_r)} \quad (14)$$

269

270 with s and r indicating saturated and residual values of the soil water
 271 content θ . The values of $K(\theta_{sat})$, m , n , θ_s and θ_r were those computed
 272 by Wosten et al. (1999) for organic topsoils. Solving the above equations
 273 resulted in a leaching rate, and by consequence in a transfer rate value of
 274 $8.1 \times 10^{-3} \text{ d}^{-1}$.

275

276 **Transfers of organic chlorine from the forest floor to the soil**
 277 (k_{42}) The leaching rate of organic chlorine from the forest floor was ex-
 278 trapolated from the organic matter balance estimated by Thiry (2010). The
 279 transfer factor k_{42} in this study is set equal to the ratio of the litterfall rate,
 280 2869 kg ha⁻¹ yr⁻¹, and the humus stock, 77259 kg ha⁻¹. This results in an
 281 annual average value of $1.01 \times 10^{-4} \text{ d}^{-1}$.

282

283 **Export through leaching of inorganic chlorine from the soil (k_{18})**
 284 Similarly to the transfer rate k_{31} , this transfer rate is estimated based on the
 285 water balance estimation in the pine stand. The thickness of the mineral soil
 286 layer is 1100 mm (Thiry, 2010) and its moisture content θ fluctuates around
 287 field capacity (Vincke and Thiry, 2008). The Mualem - van Genuchten pa-
 288 rameters ($K(\theta_{sat})$, m , n , θ_s and θ_r) values of this medium-textured soil have
 289 been taken from Wosten et al. (1999). The soil percolation Q was estimated
 290 at 277 mm yr⁻¹ since this deeper soil layer is also influenced by the pine tran-
 291 spiration (T_p), which during the sampling period was equal to 176 mm yr⁻¹
 292 (Vincke and Thiry, 2008). This resulted in a transfer rate k_{18} of 2.2×10^{-4}
 293 d⁻¹.

294
 295 **Export through leaching of organic chlorine from the soil (k_{28})**
 296 In the absence of data on chlorine speciation in groundwater, the loss of or-
 297 ganic chlorine was assumed to reflect the proportion of organic chlorine in
 298 drainage water as estimated by Öberg et al. (2005). Those authors indicated
 299 a form to total ratio of 0.01 for the organic form as opposed to 0.7 for the
 300 inorganic form of chlorine in the runoff water. The inorganic chlorine in the
 301 drainage water of the mineral soil at the stand is equal to the inorganic chlo-
 302 ride content in the soil multiplied by k_{18} . Given this and the fact that the
 303 organic chlorine content in the soil is around 401 kg ha⁻¹, the leaching rate
 304 k_{28} is estimated to be 1.21×10^{-4} d⁻¹.

305
 306 **Export through volatilisation of organic chlorine from the forest**
 307 **floor (k_{49})** The transport of volatile organic chlorine from the forest floor
 308 to the atmosphere was estimated to be within the same range as the best
 309 estimates for the forest, i.e. 1 kg ha⁻¹ yr⁻¹, suggested by Öberg et al. (2005)
 310 based on other studies. Knowing that the forest floor within the pine stand
 311 contains 26.4 kg organic chlorine, the volatilisation rate has been estimated
 312 at 1.04×10^{-4} d⁻¹.

313
 314 **Transfers from soil and forest floor to roots (k_{15} and k_{35})** These
 315 transfers reflect the contribution of root absorption to the annual tree de-
 316 mand (Thiry, 2010). Plants acquire most of their chlorine from soil solution
 317 as chloride anions (Cl-) (White and Broadley, 2001). Accordingly, the in-
 318 organic pool of chlorine in the soil was considered to be the only source of
 319 chlorine for root absorption. Chlorine uptake by the aboveground biomass
 320 was computed as the sum of the chlorine immobilisation in the perennial

compartments (wood, branches, bark) and the chlorine returns to the soil via litter-fall and through-fall. In the pine stand, this uptake has been estimated to be $13.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Thiry, 2010). In addition to this, chlorine uptake by trees includes the root consumption, i.e. $0.05 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for coarse roots (2-5 mm) and $0.97 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for fine roots ($< 2 \text{ mm}$). This results in a total tree chlorine uptake of $14.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Based on active root distribution between the forest floor and the mineral soil, the proportion of chlorine uptake by the roots from both layers was assumed equal (Vincke and Thiry, 2008). Knowing that 8.1 kg ha^{-1} inorganic chlorine were measured in the forest floor and 155 kg ha^{-1} in the soil, the average annual uptake rates k_{35} and k_{15} were estimated to be respectively $2.49 \times 10^{-3} \text{ d}^{-1}$ and $1.3 \times 10^{-4} \text{ d}^{-1}$.

Transfers from roots to soil and forest floor (k_{53} , k_{54} , k_{51} and k_{52}) In the pine stand, the roots contain 4.7 kg ha^{-1} of chlorine. The ratio between organic and inorganic chlorine in the small roots is around $0.29/0.71$ (Thiry, 2010). Small root turnover is usually considered as the main source of decomposed organic matter's return to the soil from the below-ground biomass (Vogt et al., 1996). In our model, the amount of chlorine allocated to the new small root ($< 2 \text{ mm}$), $0.97 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (see k_{15} and k_{35}), is assumed to return to the soil through decay, while the amount allocated to the growing coarse roots is assumed to accumulate in the below-ground biomass. As mentioned earlier, the proportion of chlorine uptake by the roots from the forest floor is equal to the one from the mineral soil. Based on the inventory of organic and inorganic chlorine in the small roots, the average annual transfer rates of chlorine from the root system to the different soil and forest floor pools were $1.97 \times 10^{-4} \text{ d}^{-1}$ for k_{53} and k_{51} , and $8.22 \times 10^{-5} \text{ d}^{-1}$ for k_{54} and k_{52} .

Translocation from roots to above-ground tree biomass (k_{56}) Chlorine is an essential micronutrient for plants. It was shown to be readily taken up by trees and to be highly mobile in pine trees (Thiry, 2010). The distribution pattern of chlorine in trees indicates a strong acropetal transfer with the highest chlorine concentrations measured in growing tissues; i.e. needles and twigs. In the pine stand, the transfer of chlorine from roots to the above-ground biomass was estimated to be $13.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Thiry, 2010). This flux corresponds to the translocation of chlorine taken up by roots that is not retained in tree roots. The transfer rate k_{56} is defined as the ratio between this flux and the total chlorine content in the roots, which

Table 1: *Average annual values, expressed per day, assigned to the different transfer rates k_{ij} 's*

Transfer rates	values (d^{-1})
k_{10-7}	0.29
k_{10-3}	0.71
k_{11-1}	1.0
k_{76}	0.15
k_{73}	0.845
k_{65}	1.36×10^{-3}
k_{63}	6.61×10^{-3}
k_{64}	4.93×10^{-5}
k_{56}	8×10^{-3}
k_{53}	1.97×10^{-4}
k_{54}	8.22×10^{-5}
k_{51}	1.97×10^{-4}
k_{52}	8.22×10^{-5}
k_{35}	2.49×10^{-3}
k_{31}	8.1×10^{-3}
k_{34}	6.575×10^{-4}
k_{42}	1.01×10^{-4}
k_{49}	1.04×10^{-4}
k_{21}	4.22×10^{-6}
k_{28}	1.21×10^{-6}
k_{15}	1.3×10^{-4}
k_{18}	2.2×10^{-4}

is around 4.7 kg ha^{-1} (Thiry, 2010). This results in a value of $8 \times 10^{-3} \text{ d}^{-1}$ for k_{56} .

Translocation from above-ground tree biomass to roots (k_{65})
The measurements performed at the site indicated a considerable decrease in Cl concentration in pine needles during senescence prior to leaf fall (Thiry, 2010). Chlorine appears to be highly mobile within the phloem. Accordingly, the recycling of Cl, defined as the ratio of phloem/xylem nutrient fluxes, approximates 0.2 for many plants (White and Broadley, 2001). Consequently, given an acropetal flux of $13.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (see k_{56}) and a total above-ground chlorine content of 5.5 kg ha^{-1} , a annual transfer rate of 1.36×10^{-3} was considered to represent well the translocation of Cl from aboveground pine biomass to roots.

3.3. Model evaluation and applications

Prior to studying the impact of a range of contamination scenarios on the accumulation and dispersion of ^{36}Cl within the different compartments of a pine stand system, the model was been evaluated for stable chlorine. First, the sensitivity of the model to the choice of the transfer rate values has been assessed. Next, the coherence between observed and simulated chlorine contents has been evaluated.

3.3.1. Sensitivity to transfer rates

A set of simulations was performed in order to evaluate the uncertainty related to the choice of the mean k_{ij} value on the simulated chlorine content in the system. For each simulation within the ensemble of l simulations, a random value drawn from a normal distribution with as mean value the values provided in Table 1 and a standard deviation of 20% from these mean values, was assigned to the transfer rates k_{ijl} . A standard deviation of 20% was set arbitrarily. The impact of such a 20% uncertainty is evaluated by quantifying the variability of the simulated chlorine content given this standard deviation. The standard deviation σ of the chlorine content in the system is used as a measure for the variability:

$$\sigma = \sqrt{\frac{\sum_{l=1}^n (C_l - \bar{C})^2}{n}} \quad (15)$$

where C_l is the individual simulated concentration of chlorine within the seven-compartments system for each specific k_{ijl} value, and \bar{C} is the mean of the C_l values.

In order to evaluate the role of each transfer rate on the dispersion and accumulation of the chlorine within the seven-compartment system, the correlation between the selected transfer rate k_{ij} and the chlorine content in the compartments has been computed using the determination coefficient, r :

$$r_{ij} = \frac{\sum_{l=1}^n (k_{ijl} - \bar{k}_{ij})(C_l - \bar{C})}{\left(\sum_{l=1}^n (k_{ijl} - \bar{k}_{ij})^2 \sum_{l=1}^n (C_l - \bar{C})^2 \right)^{1/2}}, \quad (16)$$

399 where k_{ij_l} are the individual values assigned to the transfer rate k_{ij} , and
400 \bar{k}_{ij} the mean of k_{ij_l} . This correlation coefficient is a direct measure of how
401 well the transfer factor k_{ij} and the concentration within the compartments
402 vary jointly. The values assigned to k_{ij_l} were a set of values around the mean
403 transfer rate provided in Section 3.2, with a range extending from -50% to
404 +50%. The sensitivity and the correlation studies were performed for both
405 underground and atmospheric chlorine supplies of $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of stable
406 chlorine after a simulation of 2000 years.

408 3.3.2. Simulations versus observations

409 As mentioned in Section 2.2, an atmospheric deposition of 12.6 kg ha^{-1}
410 yr^{-1} of stable chlorine has been observed at the pine stand (Thiry, 2010).
411 Given this rate, the simulated chlorine content is compared to the observed
412 content in the different compartments of the system. The significance of their
413 differences are evaluated and discussed in Section 4.2.

415 3.3.3. Contamination scenarios

416 Once the model had been evaluated, a range of contamination scenarios
417 were simulated to estimate the possible redistribution of ^{36}Cl between the dif-
418 ferent forest compartments. These scenarios differ from each other by their
419 source, external supply and exposure time. An external chronic atmospheric
420 supply of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ has been taken arbitrarily as the reference sce-
421 nario. Next, a chronic underground source of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ was simulated.
422 The chlorine content and partitioning within the different compartments of
423 the system for both scenarios were compared to each other to evaluate the
424 impact of the contamination source. Finally, the exposure time to an atmo-
425 spheric contamination of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ has been limited to 2000 years,
426 100 years and 1 year. The model outputs for these different scenarios have
427 been compared as well, in particular the partitioning and residence time of
428 the chlorine in the different compartment.

430 4. Results and discussion

431 4.1. Sensitivity to transfer rates

432 4.1.1. Impact of transfer rates uncertainty on chlorine accumulation in sys- 433 tem

434 The impact of the uncertainty related to the values assigned to the trans-
435 fer rates has been evaluated by quantifying the sensitivity of the simulated
436 chlorine content in the system to a 20% variation in transfer rate value. The
437 resulting normalised standard deviation from the simulated mean chlorine
438 content (in %) in each compartment, as well as in the total system, are pro-
439 vided in Table 2 for a chronic atmospheric deposition (top) and underground
440 source (bottom) of $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of stable chlorine. The sum of the stan-
441 dard deviations per compartment and per transfer rate are given as well.

442
443 Table 2 shows that an uncertainty of 20% on all transfer rates results in
444 a variability of the total chlorine content, and by consequence on the resi-
445 dence time of chlorine in the system, of around 25% for both underground
446 and atmospheric sources. In fact, the variability increases very rapidly dur-
447 ing the first 15 years of the simulations, with an average increase of $1\% \text{ yr}^{-1}$,
448 decreasing later to a roughly $0.0025\% \text{ yr}^{-1}$ (data not shown) annual increase .

449
450 The sensitivity of the model however depends on the transfer rate and
451 the chlorine source. In the case of atmospheric deposition, the total chlorine
452 content and the residence time in the system is very sensitive to a variation
453 in the transfer of inorganic Cl from the forest floor to the soil (k_{31}), and to
454 a lesser extent to a variation in the mineralisation of organic chlorine in the
455 soil (k_{21}) and a variation in the drainage of inorganic chlorine out of the soil
456 (k_{18}), resulting respectively in a variability of 13%, 11.1%, 9.9% of the total
457 content in the system given a 20% uncertainty for these transfers. For an
458 underground supply, the model is very sensitive to the value of k_{18} , and to
459 less extent to a variation in k_{21} and k_{15} (transfer from soil to roots), resulting
460 respectively in a variability of 19%, 10.2%, 10% of the total content in the
461 system. The value assigned to the transfer from the inorganic to the organic
462 chlorine pool of the forest floor (k_{34}) affects moderately the chlorine content
463 in the system.

464
465 Focussing now on the sensitivity of the individual compartments of the
466 system, Table 2 shows that under both scenarios, k_{31} , k_{18} and k_{15} have a

Table 2: *The normalised standard deviation from the mean chlorine content (in %) for each compartment given a 20% uncertainty on the transfer rates value for a chronic atmospheric deposition (top) and underground source (bottom) of 10 kg ha⁻¹ yr⁻¹ of stable chlorine, after a simulation of 2000 years.*

$k_i \setminus C_i$	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Σ	C_{tot}
k_{10-7}	<0.1	0.1	<0.1	<0.1	0.1	0.9	19.0	20.1	0.1
k_{76}	<0.1	0.1	<0.1	<0.1	0.1	0.8	<0.1	1.0	0.1
k_{65}	<0.1	0.7	0.2	<0.1	3.5	0.4	<0.1	4.8	0.6
k_{63}	0.1	1.3	0.2	0.9	2.8	17.7	<0.1	23.0	1.1
k_{64}	0.1	0.7	0.1	0.9	0.1	0.2	<0.1	2.1	0.5
k_{56}	0.1	4.3	0.9	<0.1	19.1	2.1	<0.1	26.5	3.2
k_{53}	<0.1	0.1	<0.1	<0.1	0.6	0.5	<0.1	1.2	0.1
k_{54}	0.1	0.9	0.1	1.1	0.3	0.3	<0.1	2.8	0.7
k_{51}	<0.1	0.4	0.3	0.3	0.6	0.6	<0.1	2.2	0.3
k_{52}	<0.1	2.6	0.1	0.2	0.3	0.3	<0.1	3.5	1.8
k_{35}	0.1	1.5	0.3	0.3	6.0	5.7	<0.1	13.9	1.2
k_{31}	1.8	17.7	21.5	20.2	8.5	8.1	<0.1	77.8	13.5
k_{34}	1.1	10.5	1.6	13.8	1.4	1.3	<0.1	29.7	7.8
k_{42}	0.6	9.7	0.2	11.2	0.4	0.4	<0.1	22.5	6.8
k_{49}	0.5	9.0	0.2	11.3	0.4	0.4	<0.1	21.8	7.0
k_{21}	0.4	15.4	0.1	0.1	0.3	0.3	<0.1	16.6	11.1
k_{28}	0.3	4.8	0.1	0.1	0.2	0.2	<0.1	5.7	3.6
k_{15}	0.7	9.2	7.0	7.7	14.6	14.1	<0.1	53.3	7.0
k_{18}	17.6	7.8	5.9	6.6	12.4	11.9	<0.1	62.2	9.9
Σ	23.5	96.8	38.8	74.7	71.7	66.2	19.0		76.4
k_{all}	19.8	30.2	24.9	31.9	32.1	24.1	13.8	176.8	23.1

$k_i \setminus C_i$	C_1	C_2	C_3	C_4	C_5	C_6	C_7	Σ	C_{tot}
k_{10-7}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NA	<0.1	<0.1
k_{76}	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NA	<0.1	<0.1
k_{65}	<0.1	0.9	0.2	<0.1	2.6	0.3	NA	4.0	0.5
k_{63}	0.1	2.3	0.5	1.9	3.0	18.7	NA	26.5	1.5
k_{64}	0.1	1.3	0.3	2.1	0.1	0.3	NA	4.2	0.8
k_{56}	0.1	7.4	2.0	<0.1	20.4	2.4	NA	32.3	4.4
k_{53}	<0.1	0.2	<0.1	0.1	0.6	0.6	NA	1.5	0.1
k_{54}	0.1	2.0	0.4	2.8	0.4	0.4	NA	6.1	1.1
k_{51}	<0.1	0.7	0.7	0.7	0.7	0.7	NA	3.5	0.4
k_{52}	<0.1	4.0	0.3	0.3	0.3	0.3	NA	5.2	2.2
k_{35}	<0.1	1.6	0.4	0.4	3.9	3.9	NA	10.2	1.0
k_{31}	0.5	11.8	18.8	16.0	3.5	3.5	NA	54.1	7.0
k_{34}	0.5	10.7	2.1	16.9	0.8	0.8	NA	31.8	6.1
k_{42}	0.2	6.3	0.2	9.1	0.2	0.2	NA	16.2	3.5
k_{49}	0.2	6.1	0.2	9.2	0.2	0.2	NA	16.1	3.8
k_{21}	0.2	17.6	0.2	0.2	0.2	0.2	NA	18.6	10.2
k_{28}	0.1	3.3	0.1	0.1	0.1	0.1	NA	3.8	1.9
k_{15}	0.6	16.5	16.6	16.6	16.6	16.6	NA	83.5	10.0
k_{18}	19.0	19.0	19.0	19.0	19.0	19.0	NA	114	19.0
Σ	21.7	111.7	62	95.4	72.6	68.2	NA		73.5
k_{all}	20.4	37.7	35.9	36.4	28.3	31.4	NA	190.1	26.7

467 large impact on the individual compartments. At the individual level k_{21} is
 468 the only one significantly affecting the organic chlorine pool of the soil (C_2).
 469 k_{31} has a large impact on this pool as well and on the inorganic (C_3) and
 470 organic chlorine pool of the forest floor (C_4). A 20% uncertainty on k_{31} under
 471 the atmospheric deposition scenario results in a variability of 21.5% for C_3 ,
 472 20.2% for C_4 and 17.7% for C_2 . Under the underground supply scenario, it
 473 results in a variability of 18.8%, 16.0% and 11.8%, respectively. k_{15} has a
 474 large impact on the chlorine content of the roots (C_5) and the tree (C_6). A
 475 20% uncertainty on k_{15} in both scenarios results in a variability of around
 476 15% of the chlorine content in C_5 and C_6 . Under the underground supply
 477 scenario, this parameter affects largely the content of C_2 , C_3 and C_4 as well.
 478 A variation of the k_{18} value has a large impact on the chlorine content in the
 479 drainage water (not shown in Table 2) and in the inorganic chlorine pool of
 480 the soil (C_1). A 20% uncertainty on k_{18} , under both scenarios, results in a
 481 variability of slightly less than 20% on the chlorine content in C_1 . In case
 482 of an underground supply, this parameter has also the same large impact on
 483 C_2 , C_3 , C_4 , C_5 and C_6 . Finally a 20% uncertainty on the chlorination rate in
 484 the forest floor (k_{34}) has a significant effect ($> 10\%$) on the chlorine content
 485 in C_2 and C_4 .

486
 487 On the other hand, some parameters have almost no impact on the chlo-
 488 rine content in the system and its different compartments. Under the un-
 489 derground supply scenario, the partitioning of the atmospheric deposition
 490 between leaf surface (k_{10-7}) and forest floor k_{10-3} and the partitioning of the
 491 chlorine on the leaf surface between the tree (k_{76}) and the forest floor (k_{73})
 492 have no impact on the chlorine content. However, in case of an atmospheric
 493 deposition scenario, k_{10-7} and k_{10-3} have a significant impact, 19%, on the
 494 amount of chlorine on the leaf surface (C_7). Under this scenario, k_{76} and k_{73}
 495 have no significant impact on the chlorine content. The transfer from the
 496 roots to the inorganic chlorine pool of the forest floor (k_{53}) has no signifi-
 497 cant impact under both scenarios. Other parameters such as the transfers
 498 from the tree to the roots (k_{65}) and to the organic chlorine pool of the forest
 499 floor (k_{64}), and from the roots to the organic chlorine pool of the forest floor
 500 (k_{54}) and to the inorganic chlorine pool of the soil (k_{51}) have a fairly small
 501 impact on the chlorine content. The same is valid for the drainage rate from
 502 the organic chlorine pool of the soil (k_{28}) in case of the underground supply
 503 scenario.

504

Table 2 also shows that the chlorine content of some compartments is almost uninfluenced by the value assigned to the transfer rates. This is the case of the leaf surface compartment C_7 , except under the atmospheric deposition scenario where it is significantly affected by a variation of the k_{10-7} value. The impact of transfer rate uncertainty on the chlorine content in the inorganic chlorine pool of the soil (C_1) is also fairly small. This compartment is only significantly affected by k_{18} i.e. the leaching of inorganic chlorine from the soil. The content of organic chlorine in the soil (C_2), on the other hand, is strongly affected by the values assigned to transfer rates. This compartment is the most affected by each transfer rate individually. The chlorine content in the organic pool of the forest floor (C_4), in the roots (C_5) and in the tree (C_6) compartments, which are both strongly linked, are in general quite sensitive to the different transfer rates as well.

From Table 2 it can be seen that the sum of the impact of each individual transfer rate uncertainty on the chlorine content in the system and its compartments is much larger than the impact of all transfer rate uncertainties in one simulation. This means that the system is acting as a buffer to smooth out the overall effect of variation in the transfer rates. The variation in the whole system is smaller than the variation in the individual components. By consequence, in our model, it is expected that environmental changes would have less impact at the system scale than at the individual component scale. The processes within the system interact with each other, in agreement with the high dynamics characterising the chlorine cycling.

4.1.2. Correlation between transfer rates and chlorine content in the system

The role of each transfer rate on the chlorine content within the system and its different compartments has been evaluated by quantifying the correlation between the simulated chlorine content and the transfer rate values.

The values of the Pearson correlation between the transfer rates and the chlorine content in the different compartments are provided in Table 3 for a chronic atmospheric deposition of $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of stable chlorine. The values are only mentioned for correlations with significances larger or equal to 95%. The correlation coefficients were similar for a chronic underground source (data not shown), except the correlation between the transfer rates and the leaf surface compartment C_7 . In case of underground supply, there is

Table 3: *Pearson correlation ($p < 0.05$) between the chlorine content in the different compartments and the transfer factors for a chronic atmospheric deposition of $10 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of stable chlorine, after a simulation of 2000 years.*

$k_i \setminus C_i$	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_{tot}
k_{10-7}	-1	1	-1	1	1	1	1	1
k_{76}	-0.99	0.99	-1	1	1	1		0.99
k_{65}	-1	1	-1	0.99	1	-1		1
k_{63}	0.95	-0.95	0.95	-0.95	-0.95	-0.95		-0.95
k_{64}	-1	1	-1	1	-1	-1	0.99	1
k_{56}	0.97	-0.97	0.97	-0.97	-0.97	0.97		-0.97
k_{53}	1	-1	1	-1	-1	-1	0.99	-1
k_{54}	-1	1	-1	1	-1	-1	0.99	1
k_{51}	0.99	-0.99	-0.99	-0.99	-0.99	-0.99	0.54	-0.99
k_{52}	-1	1	-1	-1	-1	-1	-0.99	1
k_{35}	-1	1	-1	1	1	1		1
k_{31}	0.96	-0.96	-0.96	-0.96	-0.96	-0.96		-0.96
k_{34}	-0.99	0.99	-0.99	0.99	-0.99	-0.99		0.99
k_{42}	0.99	0.99	0.99	-0.99	0.99	0.99		0.99
k_{49}	-0.99	-0.99	-0.99	-0.99	-0.99	-0.99		-0.99
k_{21}	0.97	-0.98	0.97	0.97	0.97	0.97		-0.98
k_{28}	-0.99	-0.99	-0.99	-0.99	-0.99	-0.99		-0.99
k_{15}	-1	1	1	1	1	1		1
k_{18}	-0.96	-0.96	-0.96	-0.96	-0.96	-0.96		-0.96

no chlorine deposition on the leaf surface, and consequently there is no correlation possible with transfer rates. In the case of atmospheric deposition, the chlorine content within this compartment is only significantly correlated with the partitioning of the deposition between leaf and forest floor compartments (k_{10-7} and k_{10-3} , and with the transfers from roots to forest floor and soil (k_{64} , k_{53} , k_{54} , k_{51} and k_{52}).

Table 3 shows that, overall, the chlorine contents and the transfer rates are strongly correlated and that the correlations between both are very linear. There are however strong differences between transfer rates and compartments regarding the sign of the correlations. The parameters that show a positive correlation with the chlorine content in C_2 ; i.e. k_{10-7} , k_{76} , k_{65} , k_{64} , k_{54} , k_{52} , k_{35} , k_{34} , k_{42} and k_{15} , show a positive correlation with the total chlorine content in the system as well, and inversely for the other parameters. This means that, based on the sensitivity analysis performed in previous section, an increase of the uptake rate of inorganic chlorine by the roots (k_{15})

558 or the chlorination rate in the forest floor compartment (k_{34}) would lead
559 to a significant increase of the total chlorine content and its residence time
560 in the system. This can be explained by the fact that an increase of the
561 chlorination process (k_{34}) in the forest floor increases the amount of chlorine
562 immobilised in the organic pools of the soil profile, and that a larger uptake
563 of inorganic chlorine by the roots (k_{15}), in particular in case of underground
564 supply, results in more substantial recycling and may contribute to an en-
565 hanced stabilisation of chlorine in the system.

566
567 On the other hand, an increase in the leaching rate from forest floor and
568 soil (k_{31} and k_{18}) and the degradation of organic compounds in the mineral
569 soil (k_{21}) would lead to a significant decrease of the total chlorine content and
570 its residence time in the system. An increase of the values assigned to k_{49} , k_{18}
571 and k_{28} , which are the fluxes through which chlorine leaves the system, log-
572 ically results in a decrease of the chlorine content in each compartment and
573 by consequence of the total chlorine content in the system. Next, a higher
574 leaching of soluble inorganic chlorine (k_{31}) in the forest floor (C_3) reduces on
575 one hand the amount of inorganic chlorine available for chlorination in C_3 ,
576 and therefore reduces the amount of chlorine in the organic pools (C_2 and
577 C_4). It also increases temporarily the inorganic chlorine content in the min-
578 eral soil (C_1) and consequently enhances the leaching of chlorine out of the
579 system. Finally, a higher degradation rate in the mineral soil (k_{21}) reduces
580 the amount of organic chlorine in the soil (C_2) and temporarily increases the
581 amount of soluble inorganic chlorine in the soil, which is very quickly leached
582 out of the system.

584 4.2. *Simulations versus observations*

585 The result of the simulations performed with the parameterisation pro-
586 vided in Table 1 and forced with a continuous atmospheric deposition of 12.6
587 kg ha⁻¹ yr⁻¹ of stable chlorine has been compared to the observed chlorine
588 content in the different compartments of the system. The times series of the
589 simulated chlorine content and percentage within the compartments of the
590 system are shown in Figure 2. The observed values are represented by black
591 dots. From Fig.2 it can be seen that the equilibrium state for the whole
592 system is reached after around 2000 years. In fact, the compartments al-
593 ready reach their equilibrium within 100 years except for the organic pool of
594 chlorine in the soil, which requires around 2000 years. This is quite similar

to the timeframe required for the soil carbon pool to reach equilibrium after disturbance (Liberloo et al., 2010; Wutzler and Reichstein, 2006). The major causes for this postponed steady-state are the chlorination of organic matter and the further evolution of organic chlorine in the soil.

In Table 4, the chlorine content in the different compartments after a simulation of 2000 years is compared to the observed values. The simulated content is in reasonable agreement with these observed values; they differ by less than 20% except the inorganic chlorine pool of the forest floor, which differ by 28%. No values were measured for the external leaf surface compartment. The simulated chlorine contents tend to underestimate the observed ones, except for the organic chlorine content in the soil, which is overestimated by 16%. Based on the correlation study in Section 4.1.2, an increase of the value assigned to k_{21} (mineralisation of organic chlorine in soil) or a decrease of the value assigned to k_{52} (return of organic chlorine to the soil through root decay) would lead to a better match between observations and simulations. As mentioned in Sections 3.2 and 4.1.1, given the large uncertainty related to the value assigned to transfers from organic to inorganic chlorine pool of the soil (k_{21}) and the fact that the model is very sensitive to this parameter, further studies on the process of degradation of organic chlorine to its inorganic form would be needed to explain this bias between observations and simulations.

Table 4: *Observed and simulated chlorine content in the different compartments for a chronic atmospheric deposition of $12.6 \text{ kg Cl ha}^{-1} \text{ yr}^{-1}$. The results are given in kg/ha for a system close to equilibrium.*

	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_{tot}
Observations	155	401	8.1	26.4	4.7	5.5	NA	NA
Simulations	144	466	5.8	21.7	4.7	4.8	0.01	647

4.3. Contamination scenarios

4.3.1. Atmospheric versus underground

In Figure 3 (top), the content and the percentage of chlorine in the different compartments of the system are represented for an atmospheric con-

622 tamination of ^{36}Cl at a rate of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$. During the first year of the
623 model simulation, most of the chlorine can be found in the inorganic pool
624 of the forest floor. During the second year of the simulations, the content
625 becomes the largest in the inorganic pool of the mineral soil. ^{36}Cl however
626 continues to accumulate in the organic pool of the soil and, after around 200
627 years of simulations, it becomes the largest pool. The system however will
628 require around 2000 years to reach its equilibrium state.

629
630 The leaf surface is the first pool to reach equilibrium (<1 year), followed
631 consecutively by the roots, the tree and the inorganic pool of the forest floor
632 compartments (50 years), the organic forest floor (75 years) and the inorganic
633 soil (100 years) compartments. The organic chlorine pool reaches its equilib-
634 rium after around 2000 years and contains 370 Bq ha^{-1} , which corresponds
635 to around 72% of the total chlorine content in the system. At equilibrium,
636 the inorganic pool of the soil is the second largest pool and represents 22% of
637 the total chlorine content. The leaf surface, the inorganic pool of the forest
638 floor, the roots and the tree represent together less than 2.5% of the total
639 chlorine content. The organic pool of the forest floor represents 3.3%.

640
641 After 2000 years of model simulation, a cumulative amount of 20×10^3
642 Bq ha^{-1} of ^{35}Cl have entered the system through atmospheric contamina-
643 tion, from which $513,7 \text{ Bq ha}^{-1}$ or 2.6% is still in the system at equilibrium.
644 Over this period, around 19500 Bq ha^{-1} of ^{36}Cl has left the system, 93.3%
645 through drainage and only 6.7% through volatilisation. At equilibrium, each
646 year $0.66 \text{ }^{36}\text{Cl Bq ha}^{-1}$ leaves the system through volatilisation, $9.16 \text{ }^{36}\text{Cl}$
647 Bq ha^{-1} through drainage of the inorganic pool of the soil and $0.16 \text{ }^{36}\text{Cl Bq}$
648 ha^{-1} through drainage of the organic pool of the soil. At equilibrium, the
649 residence time of chlorine in the system is around 51 years.

650
651 In Figure 3 (bottom), the content and the percentage of chlorine in the
652 different system compartments are represented for an underground contam-
653 ination of ^{36}Cl at the same rate of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$. Compared to the
654 atmospheric contamination shown in Fig. 3 (top), the equilibrium of the
655 whole system is reached in a quite similar periodrate. However, the time for
656 the tree compartments (C_5 and C_6) and for the inorganic pool of the soil to
657 reach their equilibrium is slightly faster, i.e. 50 years instead of 75 years. At
658 equilibrium, there is around 303 Bq ha^{-1} ^{36}Cl in the system. This represents
659 59% of the chlorine content in the system under the atmospheric deposition

scenario. During the first 600 years of the model simulation, the chlorine content is highest in the inorganic pool of the soil. After that, most of the chlorine can be found in the organic pool of the soil. However in this scenario this pool only represents 56% of the total chlorine content, instead of 72% under the atmospheric deposition scenario. This is compensated by a larger amount of chlorine in the inorganic pool of the soil, i.e. 39% of the total chlorine content instead of 22% in previous case.

Compared to an atmospheric contamination, the maximum fraction of ^{36}Cl in the roots (C_5) and tree compartments (C_6) is postponed from year 1 to year 30. A similar retardation effect (from 1 to 20 years) is observed for inorganic chlorine in the forest floor (C_3) but in the soil (C_1) the time to reach a maximum contamination is reduced from 10 to 1 year. Finally, the time to reach a maximum fraction of organic ^{36}Cl in the forest floor (C_4) is increased from 40 to 70 years.

From the $25.2 \times 10^3 \text{ Bq ha}^{-1}$ of ^{36}Cl that have entered the system through underground contamination over the 2000 years of simulation, 1.5% is still in the system. Around 19700 Bq ha^{-1} has left the system, 97.3% through drainage and only 2.7% through volatilisation. At equilibrium, each year $0.27 \text{ }^{36}\text{Cl Bq ha}^{-1}$ leaves the system through volatilisation, $9.66 \text{ }^{36}\text{Cl Bq ha}^{-1}$ through drainage of the inorganic pool of the soil and $0.07 \text{ }^{36}\text{Cl Bq ha}^{-1}$ through drainage of the organic pool of the soil. This means that compared to the atmospheric contamination scenario, proportionally slightly more chlorine leaves the system through drainage than through volatilisation. In addition, proportionally more chlorine is leached from the inorganic pool of the soil than from the organic pool. The residence time of chlorine in the system is shorter and is around 30 years.

4.3.2. Chronic versus time-limited

In Figure 4 (a), the content and the percentage of chlorine in the different compartments are represented for an atmospheric contamination of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ lasting until the equilibrium state has been reached, i.e. 2000 years. From then onwards, the total chlorine content in the system quickly decreases and is reduced by half in 220 years. The leaf surface, the inorganic chlorine pool of the forest floor, the root and the tree compartments are the first pools to be depleted of chlorine. The inorganic pools of the soil and

697 the forest floor at first decrease sharply, with 10 year and 1 year half-lives
698 respectively. This decrease however becomes less important after a few years
699 due to a gradual transfer of chlorine from the organic to the inorganic pool.
700 The half-life of the chlorine content in the root and the tree compartments is
701 around 6 years. The organic chlorine pools of the forest floor and the mineral
702 soil require respectively around 15 and 380 years to be reduced by half.

703

704 In Figure 4 (b), the content and the percentage of chlorine in the different
705 compartments are represented for a time-limited atmospheric contamination
706 of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ lasting for 100 years. At the point of time when con-
707 tamination ceases, the total chlorine content in the system is 192 Bq ha^{-1} .
708 This represents 19% of the cumulative amount of ^{36}Cl that has entered the
709 system during the contamination period and corresponds to 37% of the total
710 chlorine content of previous scenario at equilibrium. Once the contamination
711 ceases, the total content is reduced by half in 19 years. The half-lives of the
712 chlorine content in the different compartments are however similar to the
713 equilibrium scenario. As mentioned in previous section, after 100 years, the
714 chlorine content in the organic pool of the mineral soil has not yet reached
715 its equilibrium state. This pool only contains 15% of its content at equilib-
716 rium and by consequence most of the chlorine in the system is in its more
717 mobile form. This explains the much faster depletion of chlorine compared
718 to a system at equilibrium. Finally it has to be mentioned that once the
719 contamination ceases, the chlorine continues to accumulate in the organic
720 pool of the soil for 32 years, from 55 Bq ha^{-1} to 63 Bq ha^{-1} . Most of this
721 organic chlorine is drained from the forest floor into the mineral soil.

722

723 In Figure 4 (c), the content and the percentage of chlorine in the different
724 compartments are represented for a time-limited atmospheric contamination
725 of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ lasting for 1 year. At the point of time the contamination
726 ceases, the total chlorine content in the system is 9.8 Bq ha^{-1} . This rep-
727 represents 98% of the cumulative amount of ^{36}Cl that has entered the system
728 during the contamination period and corresponds to 1.9% of the total chlorine
729 content at equilibrium for a continuous contamination. Once the contami-
730 nation ceases, the total content is reduced by half in around 11 years. The
731 half-lives of the chlorine content in the different compartments are similar to
732 previous scenarios, except for tree and root compartments where the half-life
733 is shorter; 2.5 years instead of 5 years in previous scenarios. This can be
734 explained by the fact that the contamination duration under this scenario is

735 very short and that the chlorination process seems not sufficiently significant
736 to catch the chlorine circulating within the system. As mentioned in previous
737 section, after 1 year of simulation only the chlorine content on the external
738 leaf surface has reached its equilibrium state and most of the chlorine in the
739 soil is in its inorganic form. The chlorine is very quickly leached out the
740 inorganic chlorine pool of the soil. By consequence less chlorine is fixed in
741 the organic pools. This explains the shorter half-time for the whole system,
742 tree and root compartments in particular. Finally it has to be mentioned
743 that once the contamination ceases, the chlorine continues to accumulate in
744 the organic pool of the forest floor and the soil for respectively 3.5 years and
745 60 years, in the inorganic chlorine pool of the mineral soil for 3.5 years.

746

747 5. Conclusion

748 In this study, the development and the parameterisation of a model de-
749 scribing the fate of chlorine in a coniferous stand have been described. The
750 model has been evaluated for stable chlorine by performing a range of sensi-
751 tivity analyses and by comparing the simulated to a limited set of observed
752 values, followed by simulation of a set of ^{36}Cl contamination scenarios. The
753 scenarios differ from each other by external supply, exposure time and source.

754

755 From this study it can be concluded that the model is significantly sen-
756 sitive to variations in the transfer rate values and that the system is more
757 than the sum of all of its components. This highlights the relevancy of this
758 model with its different compartments. In addition, the variability of the
759 simulated chlorine content due to the uncertainty on the transfer rates is
760 bounded within an acceptable range and tends to stabilise at the equilib-
761 rium state. The model also estimates realistic values for the chlorine content
762 within the different compartments of the pine forest. The simulated chlo-
763 rine content in the system reaches its equilibrium after 2000 years, which is
764 in agreement with the timeframe required for the soil carbon pool to reach
765 equilibrium after disturbance.

766

767 The sensitivity study has shown that the chlorine content on the leaf sur-
768 faces, and to less extent the inorganic chlorine pool of the mineral soil, are
769 nearly unaffected by transfer rate uncertainty. The soil organic chlorine con-
770 tent is, on the other hand, strongly affected by the uncertainty. In general,

771 the transfers strongly affecting this compartments content strongly affect the
772 total chlorine content in the system, and consequently the residence time of
773 chlorine in the system; i.e. the leaching of inorganic chlorine from the forest
774 floor and the mineral soil, the uptake by the roots of inorganic chlorine from
775 the soil, the chlorination process in the forest floor and the degradation of
776 organic to inorganic chlorine in the mineral soil.

777

778 Based on the sensitivity and the correlation studies, an increase of the
779 chlorination rate in the forest floor would lead to a significant increase of
780 the total chlorine content and its residence time in the system by reducing
781 the amount of soluble chlorine in this layer, and increasing significantly the
782 amount of chlorine immobilised in the organic pools of forest floor and min-
783 eral soil. Similarly, a larger uptake of inorganic chlorine by the roots, in
784 particular in case of underground supply, results in a significant increase of
785 the residence time of chlorine in the system, through an enhanced recycling
786 of chlorine between vegetation and soil. On the other hand, an increase of
787 the fluxes through which chlorine leaves the system, results in a decrease of
788 the chlorine content in each compartment and by consequence of its residence
789 time in the system.

790

791 Given the large uncertainty of the value assigned to degradation of chlo-
792 rinated organic compounds in the mineral soil and the fact that the model is
793 very sensitive to this parameter, it is suggested that further studies be per-
794 formed involving detailed measurements of this parameter in order to obtain
795 a proper estimation of the chlorine accumulation in a forest ecosystem. This
796 is also valid for the leaching of inorganic chlorine from the forest floor and the
797 mineral soil, which are both strongly affected by the climatic conditions at
798 the stand. Under those conditions, since the safety of the radioactive waste
799 disposal needs to be assessed over a very long term, the effect of climate
800 change on ecological conditions (vegetation type, organic matter turnover,
801 water regime) cannot be neglected for an appropriate understanding and
802 modelling of chlorine cycling. Additional measurements would also allow a
803 thorough model validation.

804

805 Finally a range of contamination scenarios have been studied to estimate
806 the possible accumulation of ^{36}Cl within the different compartments of a pine
807 stand. For a similar contamination rate, the residence time of chlorine in the
808 system at equilibrium is around 30 years for underground contamination,

809 compared to 51 years for an atmospheric contamination. Under both scenar-
810 ios most of the chlorine leaves the system through drainage. However in the
811 case of an underground source, about two times less chlorine accumulates
812 in the system and proportionally more chlorine leaves the system through
813 drainage than through volatilisation. In addition, proportionally more chlo-
814 rine is leached from the inorganic pool of the soil than from the organic pool.
815 This can be explained by the fact that under this scenario only 56% of the
816 chlorine in the soil can be found in its organic form compared to 72% under
817 an atmospheric contamination scenario. Under the latter, the source directly
818 contaminates the forest floor, where significant portion of the inorganic chlo-
819 rine may be converted into its less mobile organic form.

820

821 Once the atmospheric contamination stops, the tree compartments, i.e.
822 leaf surface, leaves, wood and roots, requires less than 6 years to be depleted
823 by half of their chlorine. The total system however requires around 220
824 years for a system at equilibrium. Since the organic chlorine pool of the soil,
825 which influences the most the residence time of the chlorine in the seven-
826 compartments system, requires 2000 years to reach its equilibrium state and
827 its maximum content, the time required for the whole system to be depleted
828 by half of its chlorine content is strongly reduced in case of a shorter con-
829 tamination period.

830

831 A comparison of Cl biodynamics with other terrestrial ecosystems like
832 agricultural lands would be opportune. Compared to crop lands, forest
833 ecosystems are expected to have a higher capacity for internal recycling of
834 chlorine due to its perennial character, deep roots and large amount of organic
835 matter in top soil layer. Most of the compartment and fluxes depicted in this
836 forest model are valid for crop lands too; however some adaptations to the
837 concept of the model (selection, definition and number of compartments, and
838 transfers between compartments) as well as detailed measurements would be
839 required. For instance, the range over which the rate of Cl transformation
840 in soil varies with ecosystem types, is of high interest. Those processes are
841 influenced by various environmental factors that are not clearly understood
842 due to the lack of studies at the ecosystem scale (Clarke et al., 2009; Redon
843 et al., 2011).

844

845 Acknowledgments

846 That study was carried out in the frame of the cooperation contract
847 048824STR between Andra and SCK·CEN. The MATLAB code has been
848 developed in collaboration with Prof. E. Hanert from UCL/ELI/ELIe. We
849 are grateful to Dr. S. Altmann (Andra) for his help in manuscript improve-
850 ment.

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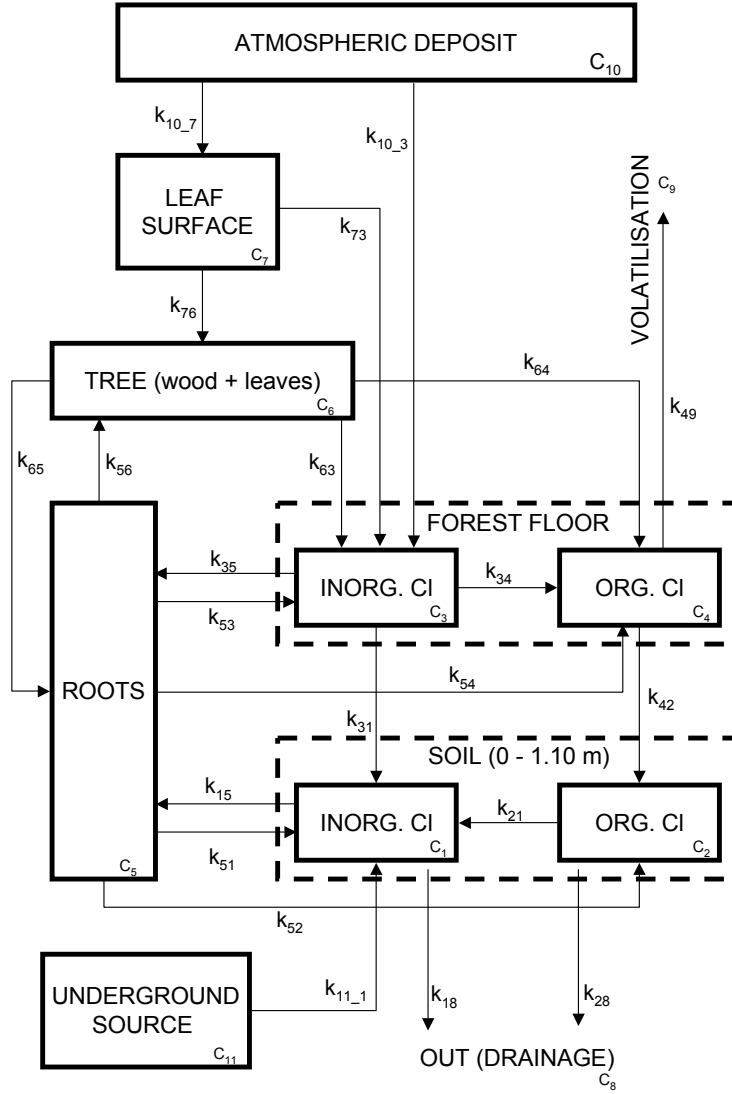


Figure 1: *Model of chlorine cycling in a coniferous forest ecosystem with rates of transfer k_{ij} between compartments C_i and C_j .*

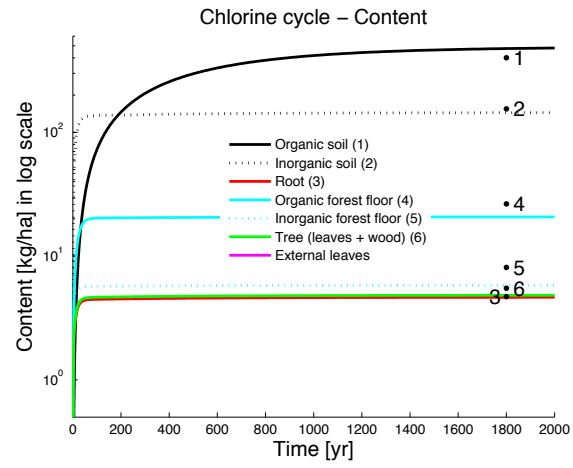


Figure 2: *Evolution over a period of 2000 years of the chlorine content (log scale) within the different compartments given a chronic atmospheric deposition of $12.6 \text{ kg Cl ha}^{-1} \text{ yr}^{-1}$.*

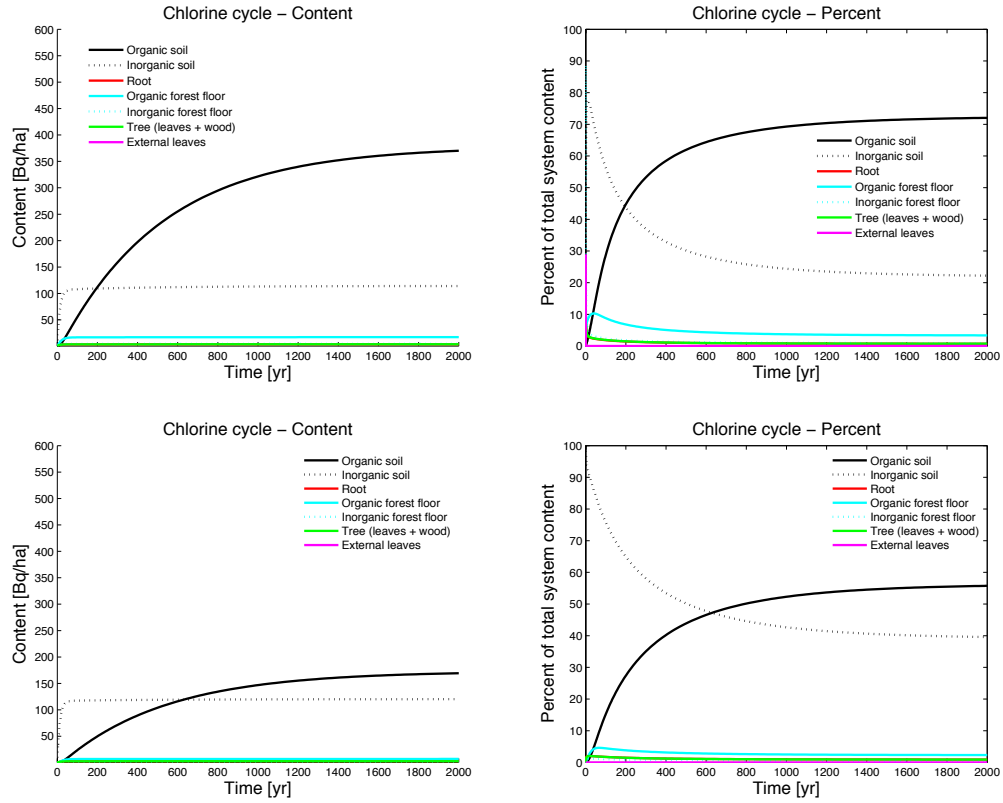


Figure 3: *Evolution over a period of 2000 years of the chlorine content and the partitioning within the compartments of the system given a chronic atmospheric contamination (top) and a chronic underground contamination of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ of ^{36}Cl (bottom).*

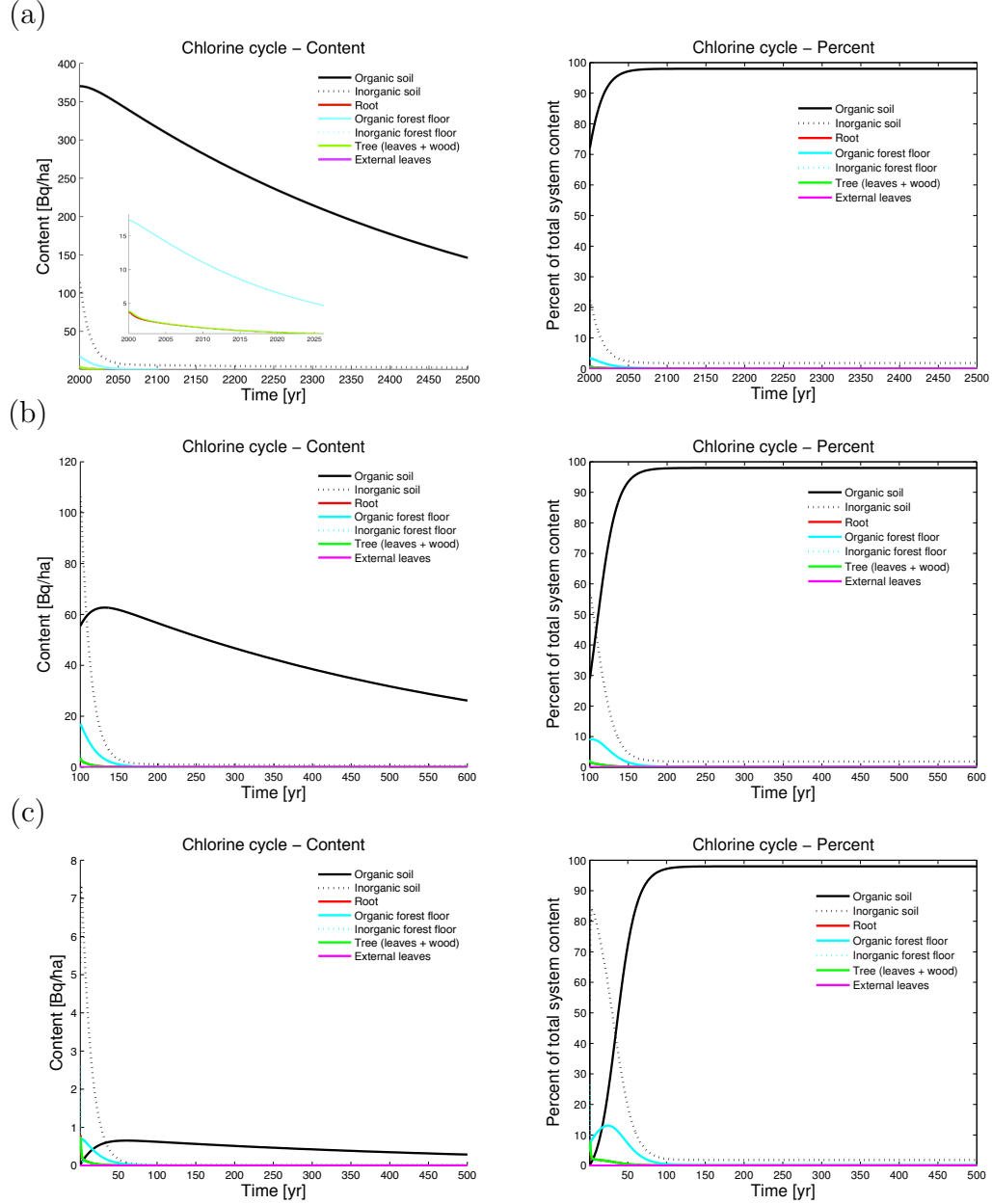


Figure 4: Evolution over a period of 500 years of the chlorine content and partitioning within the compartments once a time-limited atmospheric contamination of $10 \text{ Bq ha}^{-1} \text{ yr}^{-1}$ lasting 2000 years (a), 100 years (b) and 1 year (c) has ceased.